



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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(21) International Application Number: PCT/CA90/00284 (22) International Filing Date: 5 September 1990 (05.09.90) (30) Priority data: 403,588 6 September 1989 (06.09.89) US 573,716 27 August 1990 (27.08.90) US (71) Applicant: ALCAN INTERNATIONAL LIMITED [CA/CA]; 1188 Sherbrooke Street, West, Montreal, Quebec H3A 3G2 (CA). (72) Inventors: JIN, Iljoon ; 696 Sussex Blvd., Kingston, Ontario K7M 5B1 (CA). KENNY, Lorne, Douglas ; R.R. #2, Inverary, Ontario K0H 1X0 (CA). SANG, Harry ; 39 Faircrest Blvd., R.R. #1, Kingston, Ontario K7L 4V1 (CA).		(74) Agents: EADES, Norris, M. et al.; Kirby, Eades, Gale, Baker & Potvin, Box 3432, Station D, Ottawa, Ontario K1P 6N9 (CA). (81) Designated States: AT (European patent), AU, BE (European patent), BR, CA, CH (European patent), DE (European patent)*, DK (European patent), ES (European patent), FR (European patent), GB (European patent), IT (European patent), JP, KR, LU (European patent), NL (European patent), NO, SE (European patent). Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: LIGHTWEIGHT FOAMED METAL AND ITS PRODUCTION <div data-bbox="574 1178 1159 1633" data-label="Image"> </div> (57) Abstract <p>A method is described for producing foamed metal in which gaseous bubbles are retained within a mass of molten metal during foaming. The method comprises heating a composite of a metal matrix and finely divided solid stabilizer particles above the liquidus temperature of the metal matrix, discharging gas bubbles (21) into the molten metal composite (20) below the surface thereof to thereby form a foamed melt (22) on the surface of the molten metal composite and cooling the foamed melt thus foamed below the solidus temperature of the melt to form a solid foamed metal having a plurality of closed cells. A novel foamed metal product is also described.</p>		

DESIGNATIONS OF "DE"

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Lightweight Foamed Metal and Its ProductionBackground of the Invention

5 This invention relates to lightweight foamed metal, particularly a particle stabilized foamed aluminum, and its production.

Lightweight foamed metals have high strength-to-weight ratios and are extremely useful as load-bearing materials and as thermal insulators. Metallic foams are characterized by high impact energy absorption capacity,
10 low thermal conductivity, good electrical conductivity and high absorptive acoustic properties.

Foamed metals have been described previously, e.g. in U.S. Patent Nos. 2,895,819, 3,300,296 and 3,297,431. In general such foams are produced by adding a gas-evolving
15 compound to a molten metal. The gas evolves to expand and foam the molten metal. After foaming, the resulting body is cooled to solidify the foamed mass thereby forming a foamed metal solid. The gas-forming compound can be metal hydride, such as titanium hydride, zirconium hydride,
20 lithium hydride, etc. as described in U.S. Patent No. 2,983,597.

Previously known metal foaming methods have required a restricted foaming temperature range and processing time. It is an object of the present invention to provide a new
25 and improved metal foaming method in which it is not necessary to add a gas-evolving compound nor to conduct

the foaming in the restricted melt temperature range and restricted processing time.

Summary of the Invention

According to the process of this invention, a composite
5 of a metal matrix and finely divided solid stabilizer particles is heated above the liquidus temperature of the metal matrix. Gas is introduced into the the molten metal composite below the surface of the composite to form
10 bubbles therein. These bubbles float to the top surface of the composite to produce on the surface a closed cell foam. This foamed melt is then cooled below the solidus temperature of the melt to form a foamed metal product having a plurality of closed cells and the stabilizer particles dispersed within the metal matrix.

15 The foam which forms on the surface of the molten metal composite is a stabilized liquid foam. Because of the excellent stability of this liquid foam, it is easily drawn off to solidify. Thus, it can be drawn off in a continuous manner to thereby continuously cast a solid
20 foam slab of desired cross-section. Alternatively, it can simply be collected and cast into a wide variety of useful shapes.

The success of this foaming method is highly dependent upon the nature and amount of the finely divided solid
25 refractory stabilizer particles. A variety of such refractory materials may be used which are particulate and which are capable of being incorporated in and distributed through the metal matrix and which at least substantially maintain their integrity as incorporated rather than
30 losing their form or identity by dissolution in or chemical combination with the metal.

Examples of suitable solid stabilizer materials include alumina, titanium diboride, zirconia, silicon
35 carbide, silicon nitride, etc. The volume fraction of particles in the foam is typically less than 25% and is preferably in the range of about 5 to 15%. The particle

sizes can range quite widely, e.g. from about 0.1 to 100 μm , but generally particle sizes will be in the range of about 0.5 to 25 μm with a particle size range of about 1 to 20 μm being preferred.

5 The particles are preferably on average substantially equiaxial. They normally have an average aspect ratio (ratio of maximum length to maximum cross-sectional dimension) of no more than about 2:1. There is also a
10 relationship between particle sizes and the volume fraction that can be used, with the preferred volume fraction increasing with increasing particle sizes. If the particle sizes are too small, mixing becomes very difficult, while if the particles are too large, particle
15 settling becomes a significant problem. If the volume fraction of particles is too low, the foam stability is then too weak and if the particle volume fraction is too high, the viscosity becomes too high.

The metal matrix may consist of any metal which is capable of being foamed. Examples of these include
20 aluminum, steel, zinc, lead, nickel, magnesium, copper and alloys thereof.

The foam-forming gas may be selected from the group consisting of air, carbon dioxide, oxygen, water, inert gases, etc. Because of its ready availability, air is
25 usually preferred. The gas can be injected into the molten metal composite by a variety of means which provide sufficient gas discharge pressure, flow and distribution to cause the formation of a foam on the surface of the molten composite. It has been found that the cell size of
30 the foam can be controlled by adjusting the gas flow rate, the impeller design and the speed of rotation of the impeller, where used.

It is also possible to operate an impeller such that a vortex is formed in the molten metal composite and the
35 bubble-forming gas is then introduced into the molten metal composite via the vortex to form the gas bubbles

within the molten composite. With this batch method, the gas is slowly drawn into the melt, e.g. over a period of 10 minutes, and produces a foam in which the cells are very small, spherical-shaped and quite evenly distributed. Typically the cell sizes are less than 1 mm, compared to cell sizes of 5-30 mm when the gas is injected below the surface of the melt.

According to another method of the invention, gas is introduced into the melt by both above techniques. Thus, the gas is both injected directly beneath the surface of the melt and induced via a vortex. This makes it possible to tailor both the structure and properties of the foam.

In forming the foam according to this invention, the majority of the stabilizer particles adhere to the gas-liquid interface of the foam. This occurs because the total surface energy of this state is lower than the surface energy of the separate liquid-vapour and liquid-solid state. The presence of the particles on the bubbles tends to stabilize the froth formed on the liquid surface. It is believed that this may happen because the drainage of the liquid metal between the bubbles in the froth is restricted by the layer of solids at the liquid-vapour interfaces. The result is a liquid metal foam which is not only stable, but also one having uniform pore sizes throughout the foam body since the bubbles tend not to collapse or coalesce.

The stabilized metal foam of the present invention can form a wide variety of products. For example, it may be in the form of acoustic absorbing panels, thermal insulation panels, fire retardant panels, energy absorbing panels, electro-magnetic shields, buoyancy panels, packaging protective material, etc.

Methods and apparatus for performing the present invention will now be more particularly described by way of example with reference to the accompanying drawings, in which:

Fig. 1 illustrates schematically a first form of apparatus for carrying out the process of the invention;

Fig. 2 illustrates schematically a second apparatus for carrying out the invention;

5 Fig. 3 is a plot showing the particle size and volume fraction range over which foam can be easily produced,

Fig. 4 is a schematic illustration of a detail of foam cell walls produced by the invention.

10 Fig. 5 is a schematic illustration of a third type of foam forming apparatus.

A preferred apparatus of the invention as shown in Figure 1 includes a heat resistant vessel having a bottom wall 10, a first end wall 11, a second end wall 12 and side walls (not shown). The end wall 12 includes an
15 overflow spout 13. A divider wall 14 also extends across between the side walls to form a foaming chamber located between wall 14 and overflow spout 13. A rotatable air injection shaft 15 extends down into the vessel at an angle, preferably of 30-45° to the horizontal, and can be
20 rotated by a motor (not shown). This air injection shaft 15 includes a hollow core 16 and an impeller 17 at the lower end of the shaft. Air is carried down the hollow shaft and is discharged through nozzles 18, incorporated in the impeller blades, into the molten metal composite 20
25 contained in the vessel. Air bubbles 21 are produced at the outlet of each nozzle and these bubbles float to the surface of the composite in the foaming chamber to produce a closed cell foam 22.

This closed cell foam in the above manner continuously
30 forms and flows out of the foaming chamber over the foam spout 13. Additional molten metal composite 19 can be added to the chamber either continuously or periodically as required to replenish the level of the composite in the chamber. In this manner, the system is capable of
35 operating continuously.

The cell size of the foam being formed is controlled by adjusting the air flow rate, the number of nozzles, the

nozzle size, the nozzle shape and the impeller rotational speed.

The system shown in Figure 2 is designed to produce an aluminum foam slab with a smooth-as-cast bottom surface. This includes the same foam forming system as described in Figure 1, but has connected thereto adjacent the foam spout 13 an upwardly inclined casting table 25 on which is carried a flexible, heat resistant belt 26, preferably made of glass cloth or metal. This belt 26 is advanced by means of pulley 27 and picks up the foamed metal exiting over the foam spout 13. The speed of travel of the belt 26 is controlled to maintain a constant foam slab thickness.

If desired, the slab may also be provided with a smooth-as-cast top surface by providing a top constraining surface during casting of the slab.

In the system shown in Figure 5, the bubble forming gas is not injected directly into the melt, but is induced by way of a vortex. A crucible 35 contains a rotatable shaft 36 with an impeller 37. The crucible has a diameter of 32 cm and the impeller is rectangular, measuring about 76 mm x 127 mm.

In operation, the molten metal composite is filled to the level 32. The impeller is rotated at high speed to form a vortex 39. When a blanket of gas is provided on the surface of the melt vortex, the gas is slowly drawn into the melt to eventually form foam. The foam continues to form and fills the crucible above the melt.

Example 1

Using the system described in Figure 1, about 32 kg. of aluminum alloy A356 containing 15 vol.% SiC particulate was melted in a crucible furnace and kept at 750°C. The molten composite was poured into the foaming apparatus of Figure 1 and when the molten metal level was about 5 cm below the foam spout, the air injection shaft was

rotated and compressed air was introduced into the melt. The shaft rotation was varied in the range of 0-1,000 RPM and the air pressure was controlled in the range 14-103 kPa. The melt temperature was 710°C at the start and 650°C at the end of the run. A layer of foam started to build up on the melt surface and overflowed over the foam spout. The operation was continued for 20 minutes by filling the apparatus continuously with molten composite. The foam produced was collected in a vessel and solidified in air. It was found that during air cooling, virtually no cells collapsed.

Examination of the product showed that the pore size was uniform throughout the foam body. A schematic illustration of a cut through a typical cell wall is shown in Figure 4 with a metal matrix 30 and a plurality of stabilizer particles 31 concentrated along the cell faces. Typical properties of the foams obtained are shown in Table 1 below:

TABLE 1

Property	Bulk Density (g/cc)		
	0.25	0.15	0.05
Average cell size (mm)	6	9	25
Average Cell Wall Thickness (μm)	75	50	50
Elastic Modulus (MPa)	157	65	5.5
Compressive Stress* (MPa)	2.88	1.17	0.08
Energy Absorption Capacity* (MJ/m^3)	1.07	0.47	0.03
Peak Energy Absorbing Efficiency (%)	40	41	34

*a 50% reduction in height

Example 2

This test utilized the apparatus shown in Figure 2 and the composite used was aluminum alloy A356 containing 10 vol.% Al_2O_3 . The metal was maintained at a temperature of 650-700°C and the air injector was rotated at a speed of 1,000 RPM. Foam overflow was then collected on a moving glass-cloth strip. The glass cloth was moved at a casting speed of 3 cm/sec.

A slab of approximately rectangular cross-section (8 cm x 20 cm) was made. A solid bottom layer having a thickness of about 1-2 mm was formed in the foam.

Example 3

Using the crucible of Fig. 5, A356 aluminum alloy was melted and 15% by volume of silicon carbide powder was added thereto. The crucible was then evacuated and an atmosphere of argon was provided on the surface of the melt.

With the molten metal composite at a temperature of 650-700°C, the impeller was rotated at 1100 rpm. After 10 minutes of mixing, the composite melt started to foam. When the foam reached the top of the crucible, the impeller was stopped and samples of the foam were collected.

The foam obtained was found to have cells which were very small, spherical-shaped and quite evenly distributed. The bulk density of the foam was in the range of 1-1.5 g/cc, with an average cell size of about 250 μm and an average cell wall thickness of 100 μm .

Claims:

1. A process for producing foamed metal wherein gaseous bubbles are retained within a mass of molten metal during the foaming, comprising the steps of:

heating a composite of a metal matrix and finely divided solid stabilizer particles above the liquidus temperature of the metal matrix, forming gas bubbles within the molten composite to thereby form a foamed melt on the surface of the molten metal composite, and cooling the foamed melt below the solidus temperature of the melt to form a solid foamed metal having a plurality of closed cells.

2. A process according to claim 1 wherein gas bubbles are discharged into the molten metal composite below the surface thereof.

3. A process according to claim 1 wherein the molten metal composite is mixed to form a vortex and gas is introduced into the composite by way of the vortex whereby gas bubbles are formed within the molten metal composite.

4. A process according to claim 1 wherein the stabilizer particles are present in the metal matrix composite in an amount of less than 25% by volume.

5. A process according to claim 4 wherein the stabilizer particles have sizes in the range of about 0.1 to 100 μm .

6. A process according to claim 5 wherein the stabilizer particles have sizes in the range of about 0.5 to 25 μm and are present in the composite in an amount of 5 to 15% by volume.

7. A process according to claim 5 wherein the stabilizer particles are ceramic or intermetallic particles.

8. A process according to claim 5 wherein the stabilizer particles are metal oxides, carbides, nitrides or borides.

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9. A process according to claim 5 wherein the stabilizer particles are selected from the group consisting of alumina, titanium diboride, zirconia, silicon carbide and silicon nitride.

5 10. A process according to claim 5 wherein the stabilizer particles have an average aspect ratio of about 1:1 to 2:1.

10 11. A process according to claim 5 wherein the foamed melt is removed from the surface of the composite before being solidified.

12. A process according to claim 11 wherein the foamed melt is removed from the surface of the composite and is thereafter cast into any desired shape.

15 13. A stabilized metal foam body, comprising:
a metal matrix having dispersed therethrough a plurality of completely closed cells substantially filled with gas;

20 and finely divided solid stabilizer particles dispersed within said matrix, wherein the stabilizer particles contained in the matrix are concentrated adjacent the interfaces between the matrix metal and the closed cells.

25 14. A foam body according to claim 13 wherein the stabilizer particles are present in the metal matrix composite in an amount of less than 25% by volume.

30 15. A foam body according to claim 13 wherein the stabilizer particles have sizes in the range of about 0.1 to 100 μm .

16. A foam body according to claim 15 wherein the stabilizer particles have sizes in the range of about 0.5 to 25 μm and are present in the composite in an amount of 5 to 15% by volume.

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17. A foam body according to claim 15 wherein the stabilizer particles are ceramic or intermetallic particles.

5 18. A foam body according to claim 15 wherein the stabilizer particles are metal oxides, carbides, nitrides or borides.

10 19. A foam body according to claim 15 wherein the stabilizer particles are selected from the group consisting of alumina, titanium diboride, zirconia, silicon carbide and silicon nitride.

20. A foam body according to claim 15 wherein the closed cells have average sizes range from 250 μm and 50 mm.

15 21. A foam body according to claim 15 wherein the stabilizer particles have an average aspect ratio of about 1:1 to 2:1.

22. A foam body according to claim 15 wherein the matrix metal is aluminum or an alloy thereof.

20 23. A foam body according to claim 13 which comprises an acoustic absorbing panel.

24. A foam body according to claim 13 which comprises acoustic or thermal insulation panels.

25. A foam body according to claim 13 which comprises a fire retardant panel.

25 26. A foam body according to claim 13 which comprises an energy absorbing panel.

27. A foam body according to claim 13 which comprises an electro-magnetic shield.

30 28. A foam body according to claim 13 which comprises a buoyancy panel.

29. A foam body according to claim 13 which comprises a packaging protective material.

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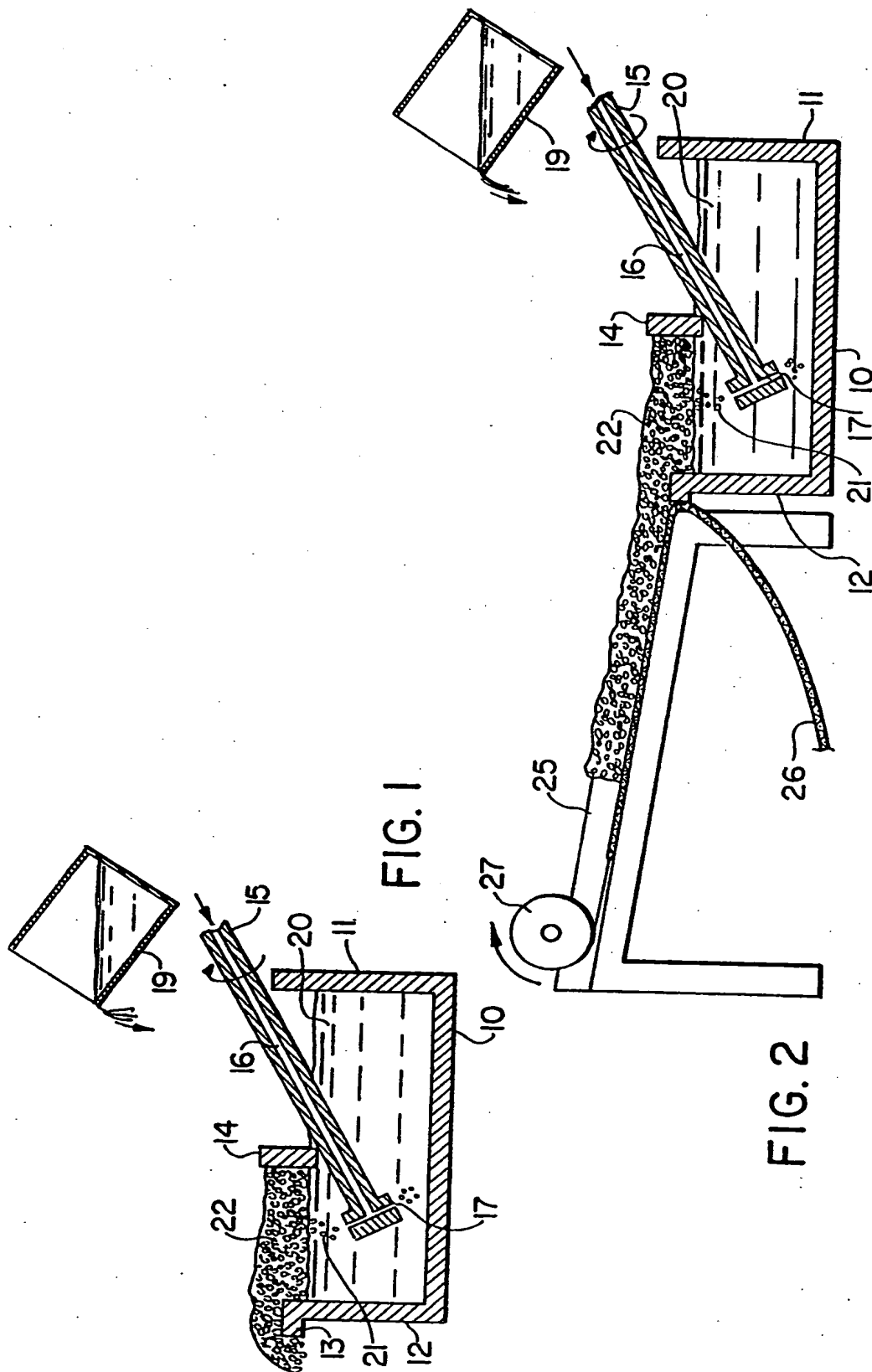


FIG. 1

FIG. 2

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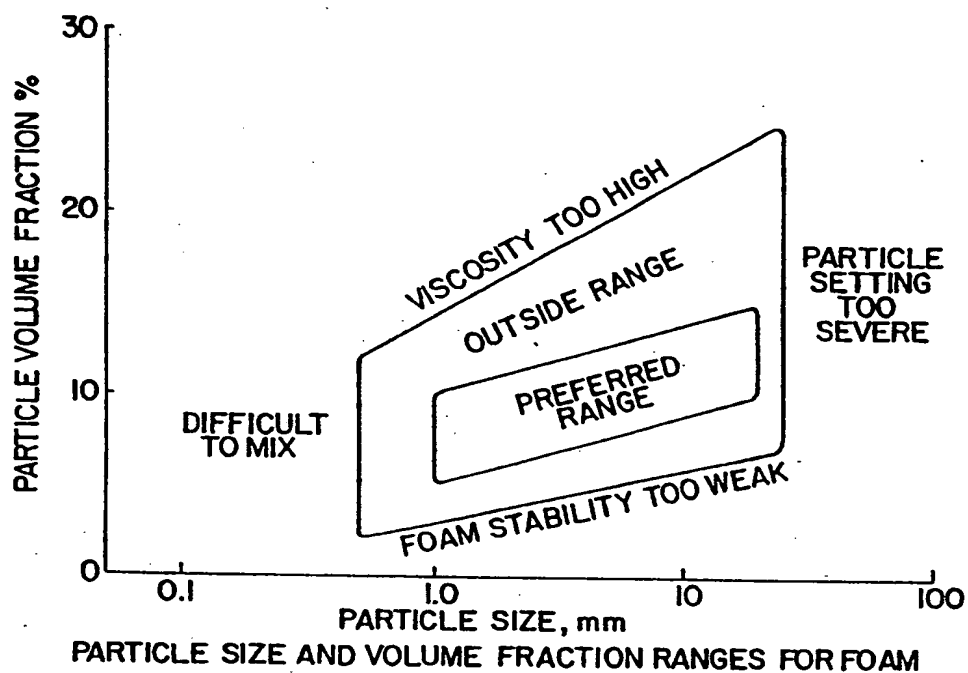


FIG. 3

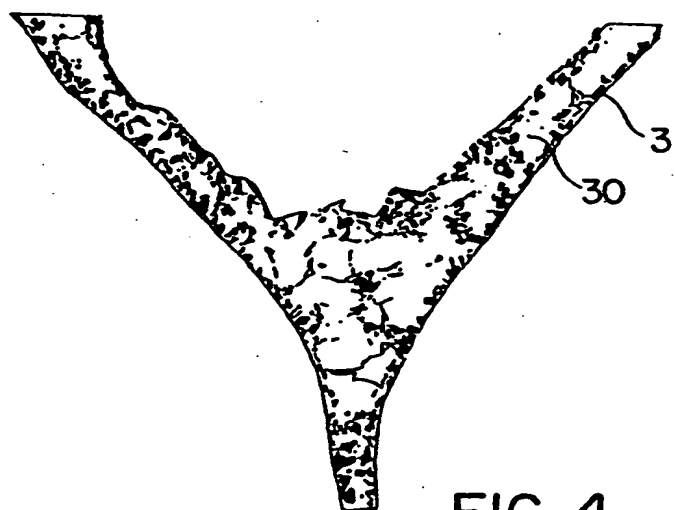


FIG. 4

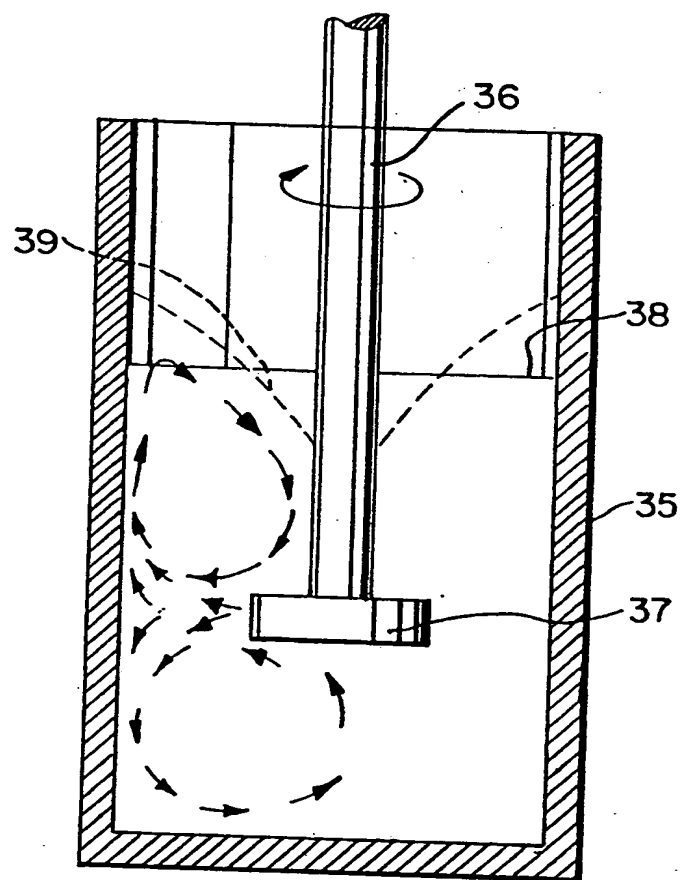
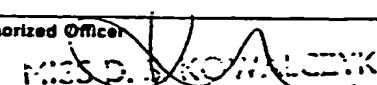
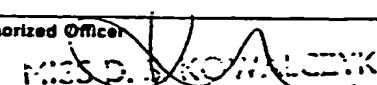
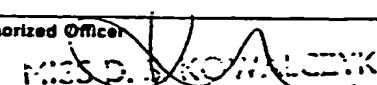


FIG. 5

SUBSTITUTE SHEET

INTERNATIONAL SEARCH REPORT

International Application No PCT/CA 90/00284

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) * According to International Patent Classification (IPC) or to both National Classification and IPC IPC ⁵ : C 22 C 1/08																				
II. FIELDS SEARCHED <div style="text-align: right; font-size: small;">Minimum Documentation Searched ⁷</div> <table style="width: 100%; border: none;"> <tr> <td style="width: 30%; border: none;">Classification System ¹</td> <td style="border: none;">Classification Symbols</td> </tr> <tr> <td style="border: none; padding-top: 10px;">IPC⁵</td> <td style="border: none; padding-top: 10px;">C 22 C 1/08</td> </tr> </table> <div style="text-align: center; font-size: x-small; margin-top: 10px;">Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸</div>			Classification System ¹	Classification Symbols	IPC ⁵	C 22 C 1/08														
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IPC ⁵	C 22 C 1/08																			
III. DOCUMENTS CONSIDERED TO BE RELEVANT ⁹ <table border="1" style="width: 100%; border-collapse: collapse; font-size: x-small;"> <thead> <tr> <th style="width: 10%;">Category ¹⁰</th> <th style="width: 70%;">Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²</th> <th style="width: 20%;">Relevant to Claim No. ¹³</th> </tr> </thead> <tbody> <tr> <td style="text-align: center; vertical-align: top;">X</td> <td style="vertical-align: top;"> US, A, 3297431 (J.A. RIDGWAY) 10 January 1967 see claims 3,5; column 2, lines 36-42; column 7, line 73 - column 8, line 37; columns 12,13; example 5; column 15, line 37 - column 16, line 2 cited in the application </td> <td style="text-align: center; vertical-align: top;">1,2</td> </tr> <tr> <td style="text-align: center; vertical-align: top;">Y</td> <td style="text-align: center; vertical-align: top;">---</td> <td style="text-align: center; vertical-align: top;">3-29</td> </tr> <tr> <td style="text-align: center; vertical-align: top;">Y</td> <td style="vertical-align: top;"> FR, A, 2282479 (PECHINEY) 19 March 1976 see claims 7,8; page 4, line 17 - page 8, line 29 </td> <td style="text-align: center; vertical-align: top;">3-29</td> </tr> <tr> <td style="text-align: center; vertical-align: top;">X</td> <td style="vertical-align: top;"> EP, A, 0210803 (SHINKO KOSEN KOGYO KABUSHIKI KAISHA) 4 February 1987 see claims 1-2,4,6; page 23, lines 14-22 </td> <td style="text-align: center; vertical-align: top;">1-2,13-29</td> </tr> <tr> <td colspan="3" style="text-align: center; vertical-align: bottom;">./.</td> </tr> </tbody> </table> <div style="font-size: x-small; margin-top: 10px;"> <div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>¹⁰ Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"A" document member of the same patent family</p> </div> </div> </div>			Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³	X	US, A, 3297431 (J.A. RIDGWAY) 10 January 1967 see claims 3,5; column 2, lines 36-42; column 7, line 73 - column 8, line 37; columns 12,13; example 5; column 15, line 37 - column 16, line 2 cited in the application	1,2	Y	---	3-29	Y	FR, A, 2282479 (PECHINEY) 19 March 1976 see claims 7,8; page 4, line 17 - page 8, line 29	3-29	X	EP, A, 0210803 (SHINKO KOSEN KOGYO KABUSHIKI KAISHA) 4 February 1987 see claims 1-2,4,6; page 23, lines 14-22	1-2,13-29	./.		
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IV. CERTIFICATION <table style="width: 100%; border: none;"> <tr> <td style="width: 50%; border: none; padding-bottom: 5px;"> Date of the Actual Completion of the International Search <div style="text-align: center;">18th December 1990</div> </td> <td style="width: 50%; border: none; padding-bottom: 5px;"> Date of Mailing of this International Search Report <div style="text-align: center;">22 JAN 1991</div> </td> </tr> <tr> <td style="width: 50%; border: none; padding-top: 5px;"> International Searching Authority <div style="text-align: center;">EUROPEAN PATENT OFFICE</div> </td> <td style="width: 50%; border: none; padding-top: 5px;"> Signature of Authorized Officer <div style="text-align: center;">  </div> </td> </tr> </table>			Date of the Actual Completion of the International Search <div style="text-align: center;">18th December 1990</div>	Date of Mailing of this International Search Report <div style="text-align: center;">22 JAN 1991</div>	International Searching Authority <div style="text-align: center;">EUROPEAN PATENT OFFICE</div>	Signature of Authorized Officer <div style="text-align: center;">  </div>														
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International Searching Authority <div style="text-align: center;">EUROPEAN PATENT OFFICE</div>	Signature of Authorized Officer <div style="text-align: center;">  </div>																			

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category *	Citation of Document, " with indication, where appropriate, of the relevant passages	Relevant to Claim No.
A	US, A, 3816952 (L.M. NIEBYSKI) 18 June 1974 see claim 42 ---	1
A	FR, A, 1259163 (LOR CORPORATION) 13 March 1961 see abstracts 17-20 -----	1

**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO.**

CA 9000284
SA 39736

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 11/01/91. The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A- 3297431		None	
FR-A- 2282479	19-03-76	None	
EP-A- 0210803	04-02-87	JP-A- 62171916	28-07-87
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US-A- 3816952	18-06-74	None	
FR-A- 1259163		None	